



TITLE:

The Chemistry on Diterpenoids in 1978. Part-I

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Review

The Chemistry on Diterpenoids in 1978. Part-I¹⁾

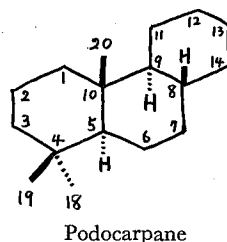
Eiichi FUJITA*, Kaoru FUJI, Yoshimitsu NAGAO, and Manabu NODE

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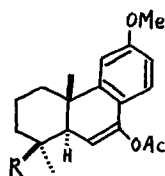
I. INTRODUCTION

This is one of a series of our annual reviews on diterpenoids chemistry. The classification of the compounds is the same as that adopted in our reviews since 1969. This review covers the literatures published between January and June 1978 and also omissions in 1977.

II. PODOCARPANE DERIVATIVES

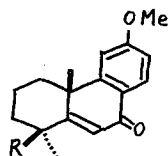


Treatment of enol acetates **1** with thallium (I) acetate and iodine gave the α,β -unsaturated ketones **3** (63%), and ketone **5** (37%). The methyl ester **2** on the same treatment gave **4** (88%).²⁾



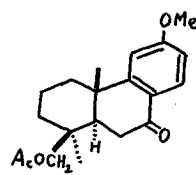
(1) $R = \text{CH}_2\text{OAc}$

(2) $R = \text{CO}_2\text{Me}$



(3) $R = \text{CH}_2\text{OAc}$

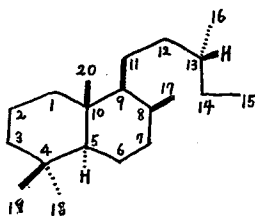
(4) $R = \text{CO}_2\text{Me}$



(5)

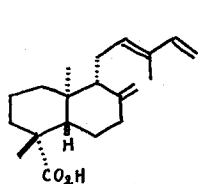
* 藤田栄一, 富士 薫, 長尾善光, 野出 学: Laboratory of Physiological Activity, Institute for Chemical Research, Kyoto University, Uji, Kyoto-Fu 611, Japan.

III. LABDANE DERIVATIVES

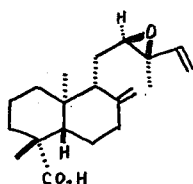


Labdane

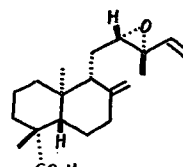
From the roots of *Mikania pyramidata* were isolated three new labdane derivatives 6, 7, and 8 together with the known other diterpenes and some new sesquiterpenes.³⁾ The structures of labdanic diterpenes 9, 10, and pumiloxide (11), isolated from the oleoresin of *Pinus pumila*, were determined.⁴⁾



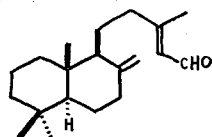
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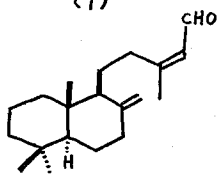
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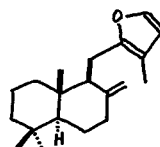
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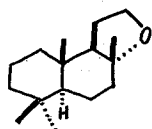


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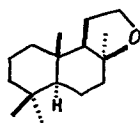


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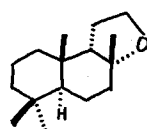
The stereochemistry of sclareol conversion products, bicyclohomofarnesene oxides 12–14, was confirmed by NMR and mass spectral determinations.⁵⁾ Mass spectra of sclareol (15) and 13-episcclareol diacetates were discussed.⁶⁾



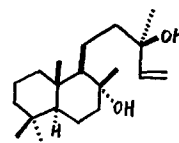
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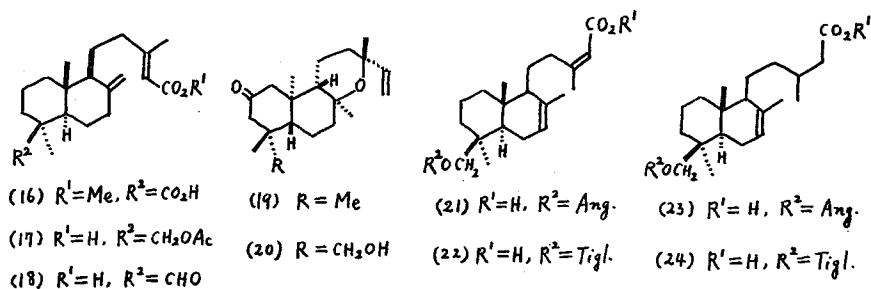


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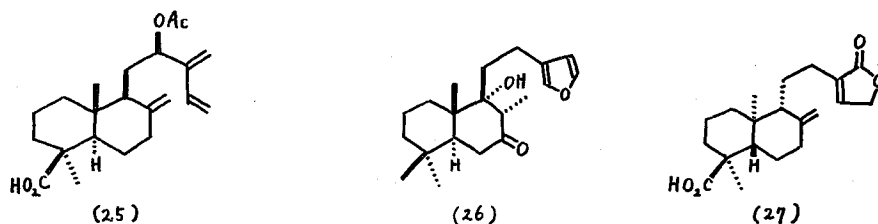


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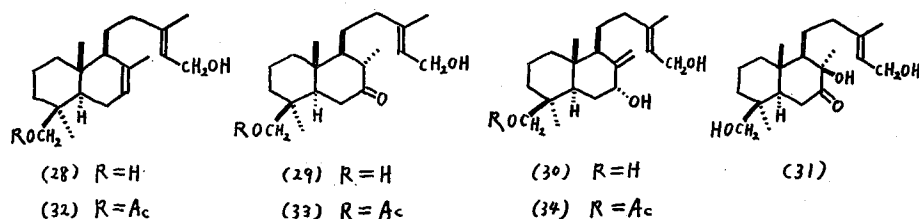
Isolation of 15-methyl agathate (16), agatholic acid acetate (17), and agathalic acid (18) from Manila copal was reported.⁷⁾ Two manoyl oxides, 19 and 20, were isolated from the aerial parts of the South African compositae *Printzia laxa* together with some new clerodane type diterpenes.⁸⁾ The structures of four new labdane type diterpenes, 21–24, in several *Brickellia* species were determined by spectroscopic methods.⁹⁾ The chemotaxonomic aspects were also discussed briefly.



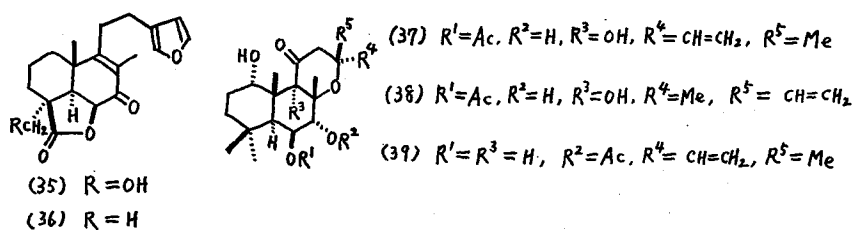
The structure of (12R)-12-acetoxymyrceocommunic acid (25), isolated as its methyl ester from *Juniperus phoenicea*, was elucidated by the spectroscopic studies and synthesis from methyl *trans*-communate.¹⁰⁾ The structure and absolute configuration of hispanolone (26), isolated from *Ballota hispanica*, were reported.¹¹⁾ Nivenolide (27) was isolated from *Croton niveus*.¹²⁾



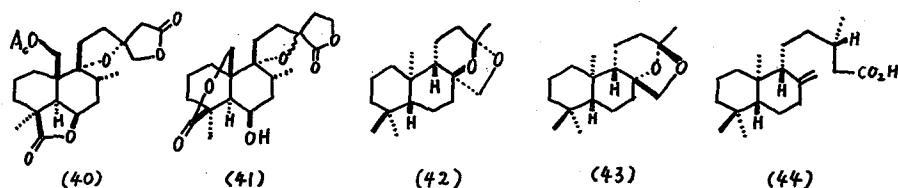
From the aerial parts of *Sideritis chamaedryfolia* seven new labdane type diterpenes, villenol (28), villenolone (29), villenatriol (30), their 19-acetyl derivatives (32, 33, and 34), and villenatriolone (31), were isolated.¹³⁾



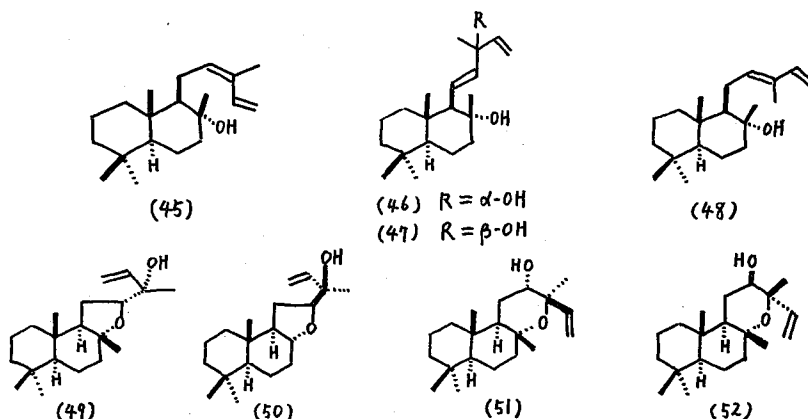
The structure of 18-hydroxyballonigrin (35), isolated from *Ballota acetobulosa*, was established by spectroscopic data and an interrelationship with ballonigrin (36).¹⁴⁾ Coleonol B (37), coleonol C (38), and deoxycoleonol (39) were isolated from *Coleus forskohlii*.¹⁵⁾



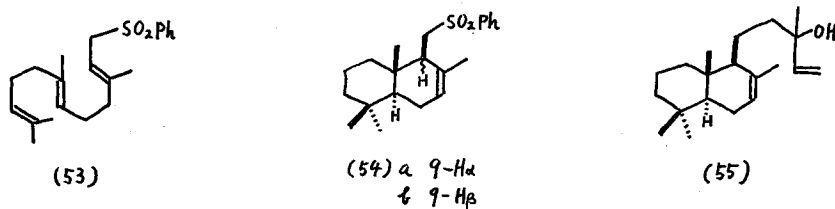
A diterpenoid, leonitin, obtained from *Leonotis leonitis*, was identified as 20-acetoxy-9,13-epoxylabda-6(19),16(15)-diol dilactone (40), which was related to nepetaefolinol (41) from *L. nepetaefolia*.¹⁶⁾



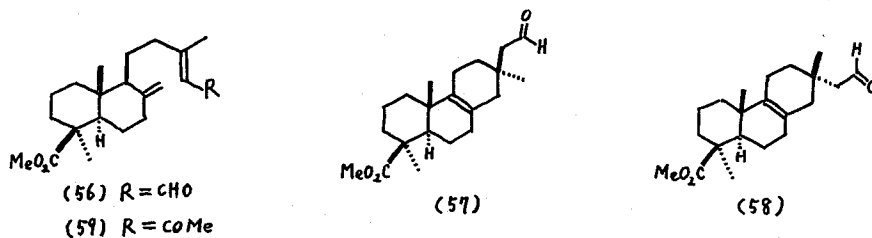
Compounds 42 and 43 were derived from eperuic acid (44) and their olfactory properties were compared with those of the corresponding enantiomers.¹⁷⁾ Sensitized photo-oxygenation of (12Z)-abienol (45) was performed to yield, after reduction, labdadienediols (46 and 47) and other oxidized labdanoids including some tobacco constituents.¹⁸⁾ Oxidation of (12-E)-abienol (48) by *m*-chloroperbenzoic acid in CHCl_3 gave four epoxyabdenols 49-52.¹⁹⁾



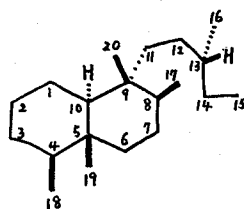
The cyclization of farnesyl phenyl sulfone (53) with SnCl_4 in benzene gave a drimane-type compound 54, which was converted to diastereomers of (\pm)-labda-7,14-dien-13-ol (55).²⁰⁾



Cyclization in formic acid of methyl labda-8(17),13-dien-15-al-19-oate (56) afforded a mixture of two aldehydes, 57 and 58, of the pimaric and isopimaric series. Similar results were found for the cyclization of the corresponding methyl ketone 59.²¹⁾

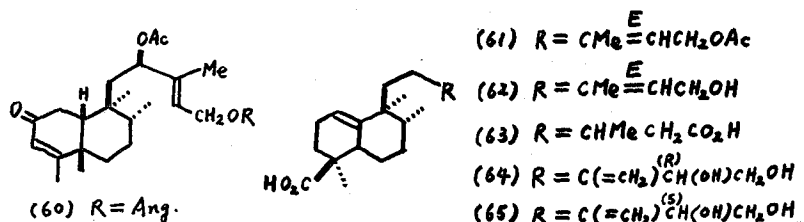


IV. CLERODANE DERIVATIVES

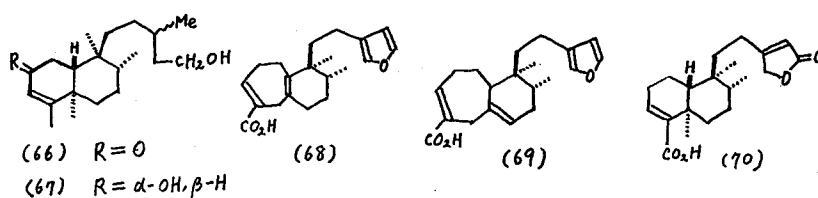


Clerodane

A new diterpene, linarienone (60), was isolated from the ether-soluble portion of the fresh subterranean part of *Linaria japonica*.²²⁾ Five new diterpene acids (61–65) were isolated as their methyl esters from *Halimium umbellatum* and their structures were determined on the basis of their spectral data and by chemical correlations.²³⁾

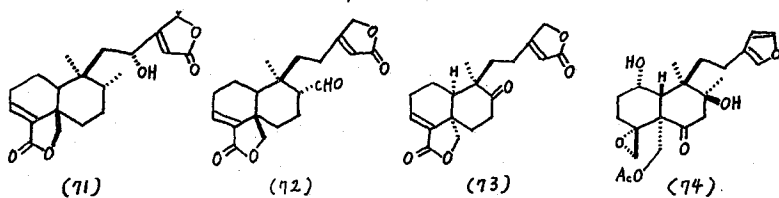


Two new clerodanic diterpenes, 66 and 67, were isolated from *Cistus populifolius*.²⁴⁾ Two clerodane type diterpenes (68 and 69) having a new carbon skeleton and a normal clerodane compound 70 were obtained from *Printzia laxa*.⁸⁾ The structures were elucidated by spectroscopic methods.

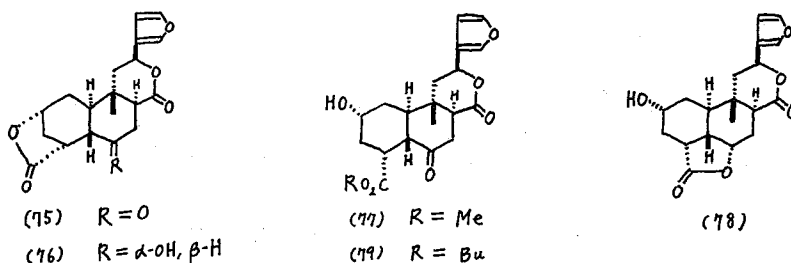


From the flowers and leaves of *Leonurus marrubiastrum*, two new diterpenes, marrubiastrol (71) and aldehydomarrubialactone (72), and the norditerpene demethylmarrubiaketone (73) were isolated. Their structures were assigned mainly by

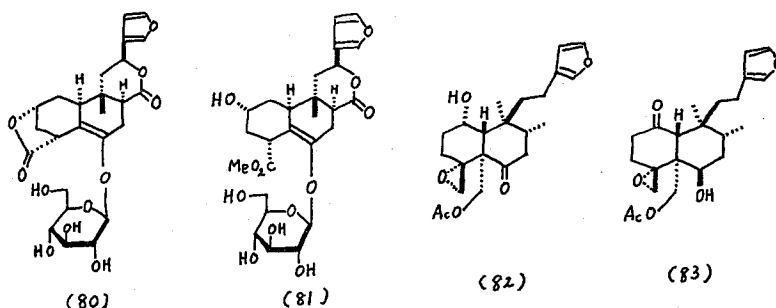
spectroscopic methods.²⁵⁾ The structure of **73** was established finally by X-ray diffraction method.²⁶⁾ 8 β -Hydroxyfruticolone (**74**), was isolated from *Teucrium eruticans*.²⁷⁾



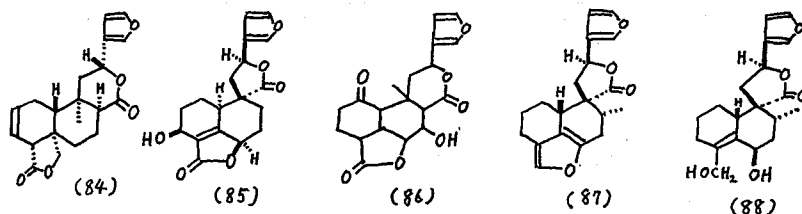
Diosbulbin D (**75**), E (**76**), F (**77**), G (**78**), and H (**79**) were isolated from *Dioscorea bulbifera* and their structures determined by spectroscopic data and chemical correlations.²⁸⁾ An X-ray analysis of diosbulbin G (**78**) was also reported.²⁹⁾



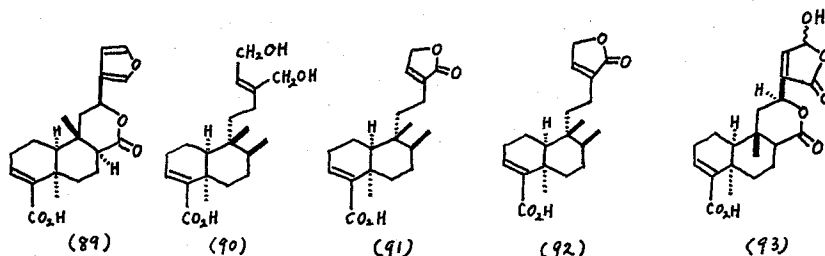
Two furanoid norditerpene glucosides, diosbulbinosides D (**80**) and F (**81**), were isolated from the fresh root tubers of *Dioscorea bulbifera* forma *spontanea*.³⁰⁾ Fruticolone (**82**) and isofruticolone (**83**) were obtained from *Teucrium fruticans* and their structures were determined by a combination of spectroscopic and X-ray analyses.³¹⁾



The structure of salviarin (**84**), a new diterpene from *Salvia splendens*, was elucidated by spectroscopic and X-ray methods.³²⁾ Teuflidin (**85**), a new norclerodane diterpene, was isolated from *Teucrium flavum*.³³⁾ The structure of trinosporide (**86**), a diterpene isolated from the fresh stems of *Trinospora cordifolia*, was assigned on spectral grounds.³⁴⁾ Montanin A (**87**) and B (**88**), new furanoid diterpenes of nor-clerodane type, were isolated from *Teucrium montanum*, and their structures were elucidated.³⁵⁾

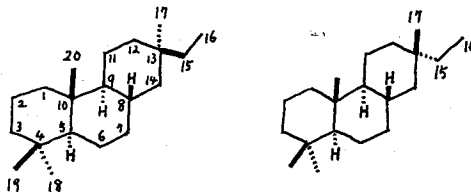


Floribundic acid (89), floridioric acid (90), floridolide A (91) and B (92), and a hydroxy-lactone 93 were isolated from *Evodia floribunda* and their structures were reported.³⁶⁾

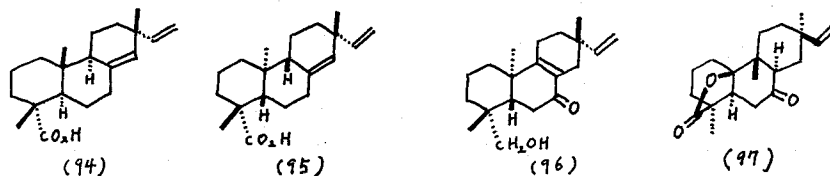


In a review on the chemical ecology, clerodane type diterpenes were cited.³⁷⁾

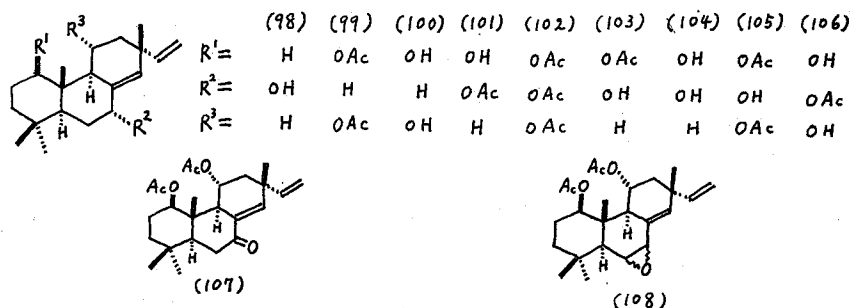
V. PIMARANE AND ISOPIMARANE DERIVATIVES



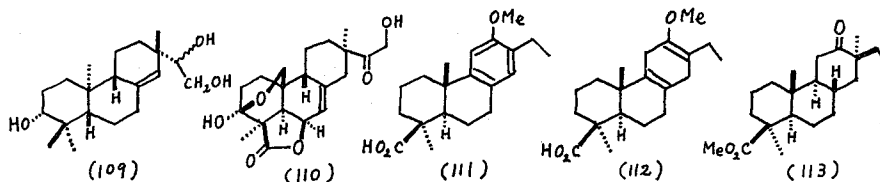
Isolation of sandaracopimaric acid (94) from Manila copal was reported.⁷⁾ *ent*-8(14),15-Pimaradien-19-oic acid (95) was isolated as the methyl ester from *Mikania pyramidata*.³⁾ A pimarane-derivative 96 was obtained from *Senecio hypchoerideus*.³⁸⁾ Assignment of the ¹³C NMR signals of rosenonolactone (97) obtained biosynthetically from sodium [1,2-¹³C] acetate was performed utilizing the ¹³C-¹³C couplings.³⁹⁾



From two *Zexmenia* species several new sandaracopimaradiene derivatives (98–108) were isolated and their structures were elucidated by spectroscopic and chemical methods.⁴⁰⁾

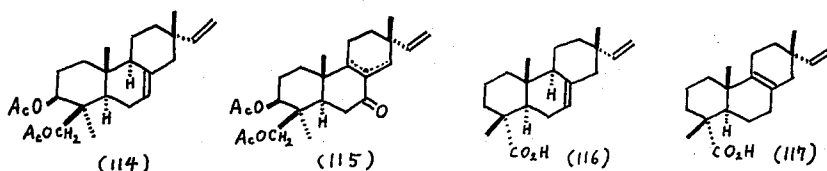


The structure of darutigenol (**109**) isolated from *Palafoxia arida* was reported.⁴¹⁾ A single-crystal X-ray analysis of annonalide, a pimaradienic diterpene from *Annona coriacea*, was undertaken, and the stereochemistries of C-9 and C-13 assigned previously were revised. Thus, its structure and stereochemistry were established as formula **110**.⁴²⁾

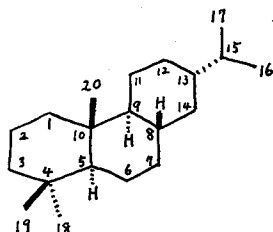


In an approach to the synthesis of the rosenonolactone type compounds, 13-ethyl-O-methylpodocarpic acid (**111**) was transformed by a Birch reduction into a compound **112**. The compound **112** was converted to ketone **113** via several steps.⁴³⁾

In attempts to induce the pimarane-cassane ring system transformation, the 7-oxo derivative **115**, derived from virescenol B 3,19-diacetate (**114**) via a few steps, was treated with BF_3 -etherate. The compound **115** however did not rearrange to a cassane-type diterpene.⁴⁴⁾ The kinetics of isomerization of **116** to $\Delta^{8(9)}$ -isopimaric (**117**), and sandaracopimaric acid (**94**) were determined at 230, 240, and 250°. A mechanism was proposed.⁴⁵⁾

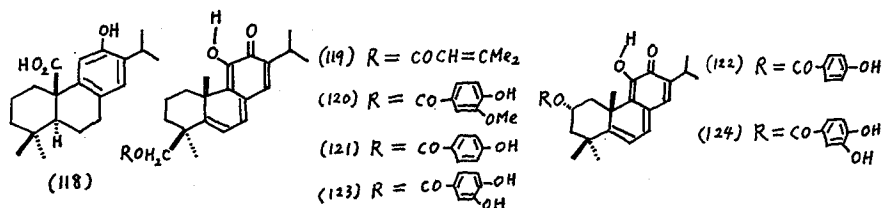


VI. ABIETANE DERIVATIVES

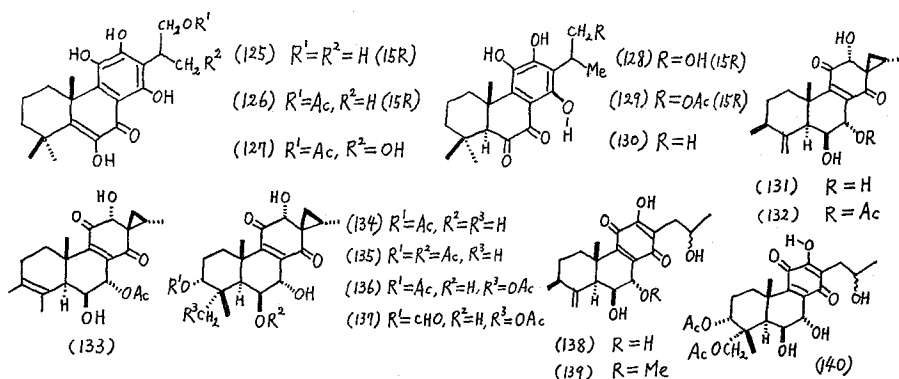


Abietane

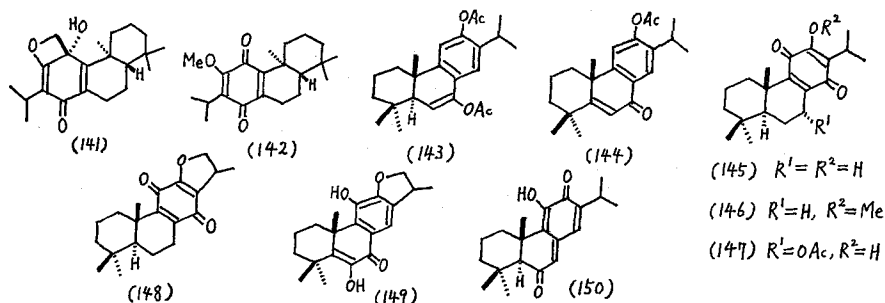
The structure of pisiferic acid (118), isolated from *Chamacyparis pisifera*, was confirmed by spectral and chemical methods.⁴⁶⁾ From *Plectranthus parviflorus*, six new *p*-quinomethanes were isolated. They are parviflorone A (119), B (120), C (121), D (122), E (123), and F (124).⁴⁷⁾



The structures of sixteen diterpenoids from *Coleus coerulescens* have been determined. They are coleon C (125), 16-O-acetyl-coleon C (126), coleon W (127), coleon D (128), 16-O-acetyl-coleon D (129), coleon V (130), 7,12-bis(O-desacetyl)-coleon N (131), 12-O-desacetyl-coleon N (132), coleon O (133), 6,12-bis(O-desacetyl)-coleon R (134), 12-O-desacetyl-coleon R (135), coleon Y (136), 3-O-desacetyl-3-O-formyl-coleon Y (137), and the abeo-compounds 138, 139 and 140.⁴⁸⁾



The structure of oxetanol compound 141 derived from royleanon methyl ether 142 by photolysis was established using X-ray analysis.⁴⁹⁾ On the reaction of enol acetates with TIOAc-I_2 , abietane type enol acetate 143 was converted to α,β -unsaturated ketone 144 (74%).²⁾ Photolysis of diterpenoid quinones 145-147 was investigated in detail.⁵⁰⁾ Dehydrocycloyleanone (148), a degradation product obtained from lycokanthol (149), has been synthesized from podocarpic acid.⁵¹⁾



In connection with studies leading to the total synthesis of taxodione (**150**), synthesis of methyl 12-oxopodocarpa-5,9(11)-diene-8 β -carboxylate (**151**) has been published.⁵²⁾ The synthetic route involving a BC \rightarrow ABC approach for the construction of this tricyclic system is shown in Chart 1.

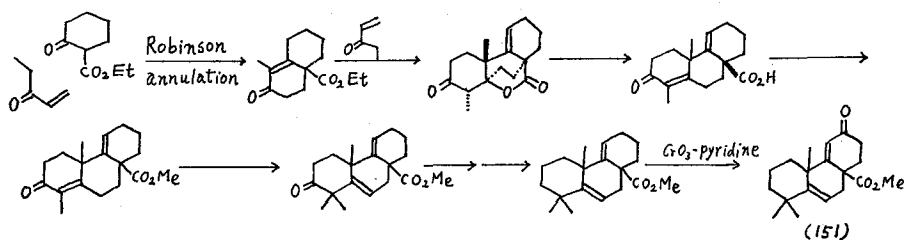
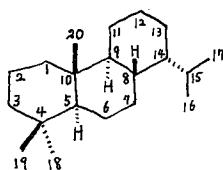


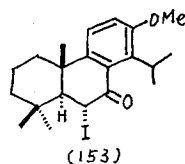
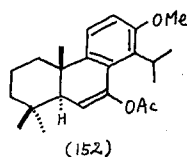
Chart 1

VII. TOTARANE DERIVATIVES

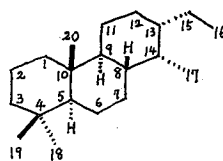


Totarane

In a paper on the reaction of enol acetates with TiOAc-I_2 , a conversion of totarane type enol acetate **152** into α -iodo-ketone **153** (76%) was reported.²⁾



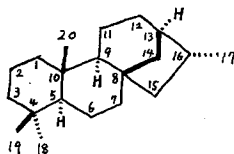
VIII. CASSANE DERIVATIVES



Cassane

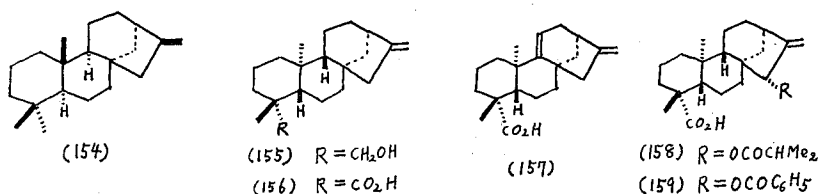
A pimarane-cassane ring system transformation was attempted. The pimarane derivative **115** on treatment with BF_3 -etherate, however, did not rearrange to a cassane-type diterpene.⁴⁴⁾

IX. KAURANE DERIVATIVES

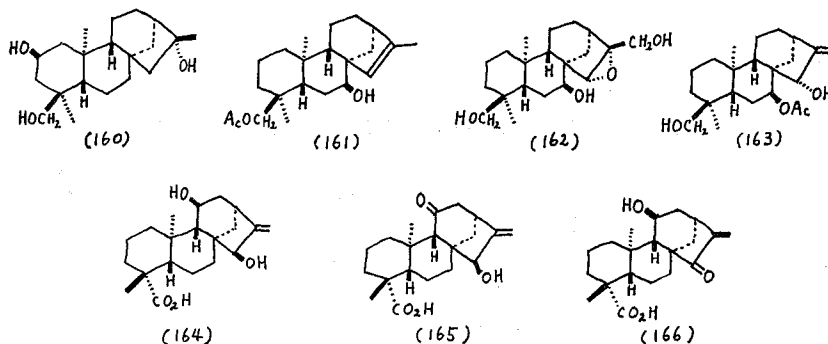


Kaurane

A mineral diterpene, bombiccite found in lignite mines has been assigned the structure of 13β -16-epikaurane (**154**) by crystal structure analysis.⁵³⁾ A known diterpenoid, *ent*-kaur-16-en-19-ol (**155**) has been isolated together with beyerane type diterpenoids from *Helichrysum dendroideum*.⁵⁴⁾ From *Zexmenia hispida*, two known diterpenoids **156** and **157** have been isolated together with new isopimaradiene type diterpenoids.⁴⁰⁾ Two new kaurenic acid derivatives **158** and **159** have been isolated from the roots of *Mikania cordata*.³⁾

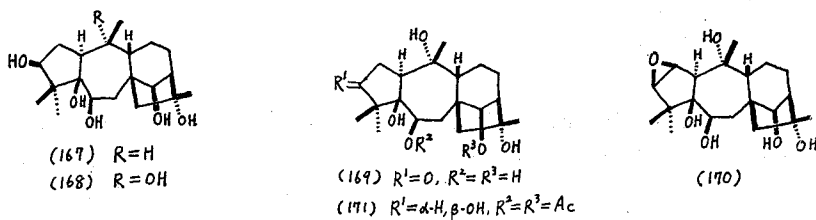


A new diterpene alcohol, *ent*-2 α , 16S, 18-trihydroxykaurane (**160**) was isolated from *Pteris ryukyuensis*.⁵⁵⁾ Two new diterpenes, sideripol (**161**) and epoxysideritriol (**162**) were isolated from *Sideritis sicula* with the known diterpene eubol (**163**).⁵⁶⁾ Three kaurenic acid derivatives **164**, **165**, and **166**, previously isolated from *Eupatorium album*, were isolated from *Adenostemma caffrum*. This fact indicates a close relationship between these two genera (*Eupatorium* and *Adenostemma*).⁵⁷⁾

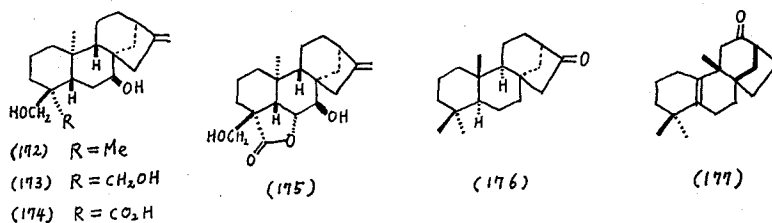


Thin-layer chromatographic and spectroscopic characterization of some diterpenes of the grayanotoxin type was reported.⁵⁸⁾ It was shown that the 20-methyl group of α -dihydroxygrayanotoxin-II (**167**) is in the β -configuration, which is in accord with the 20-methyl configuration of grayanotoxin-I.⁵⁹⁾ The chemical conversions of

grayanotoxin-III (168) to grayanotoxin-V (169), rhodjaponin-III (170), and rhodjaponin-IV (171) were published.⁶⁰⁾



The microbiological transformations of epicandicandiol (172) into *ent*-7 α , 18, 19-trihydroxykaur-16-ene (173) and *ent*-7 α , 18-dihydroxykaur-16-en-19-oic acid (174) by *Gibberella fujikuroi* were observed. But no transformation into 7, 18-dihydroxykaurenolide (175) was observed.⁶¹⁾ 17-Nor-13 β -kauran-16-one (176) on treatment with thallium trinitrate (TTN) in acetic acid gave an oxidatively rearranged product 177.⁶²⁾



A paper on the construction of the C/D ring systems of chasmanine (178) and napelline (179) was published.⁶³⁾ The central "nordenudatine" type intermediate 181 was synthesized from the quinone 180 and was then modified to the "chasmanine" model compound 182 and to the "napellin" model compound 183, as shown in Chart 2.

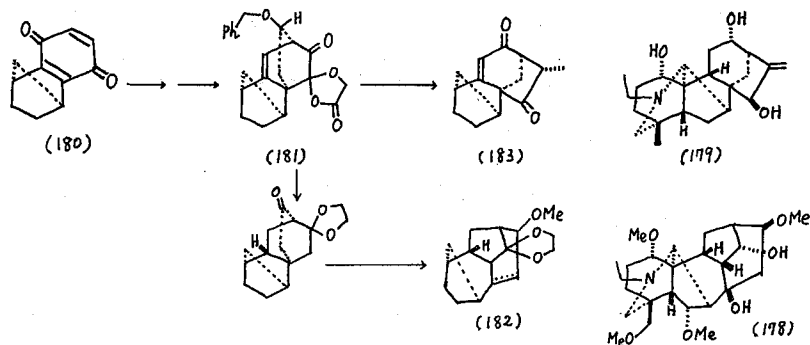


Chart 2

The syntheses of 13 β -kaur-15-ene (isophyllocladene) (184) and 13 β -kaur-16-ene (phyllocladene) (185) were achieved.⁶⁴⁾ The sequence is shown in Chart 3.

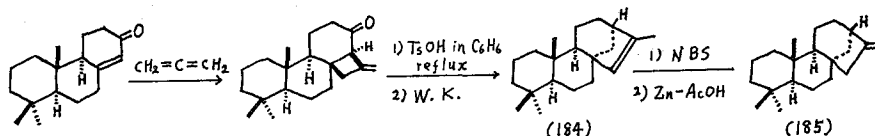


Chart 3

The total synthesis of *rac*-kaur-16-ene-11 α , 15 α -diol (188) via a sequence of reactions including the Birch reduction of alcohol 186 and the Claisen rearrangement of vinyl ether 187 as key steps was achieved. The outline is shown in Chart 4.⁶⁵⁾

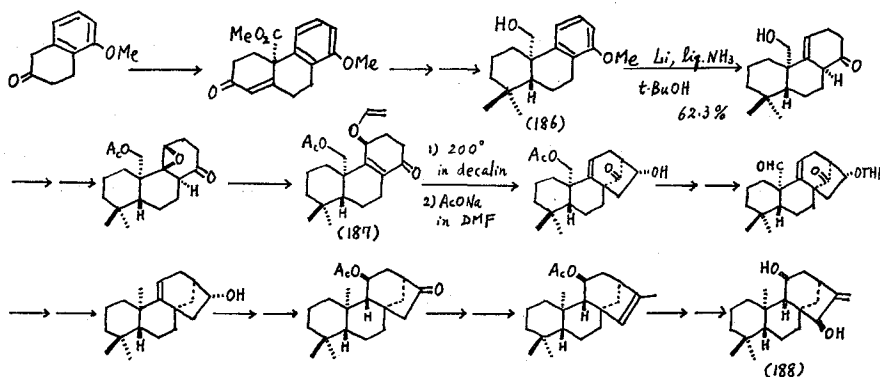
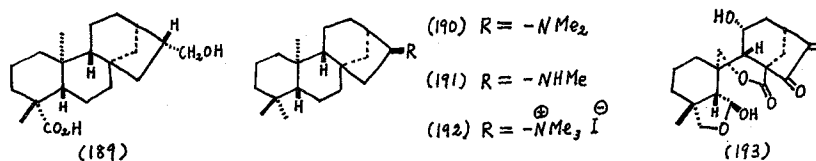


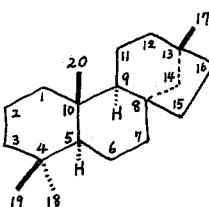
Chart 4

It was shown that the biosynthesis of hydroxy kaurenoic acid (189) by *Beyeria calycina* involved a hydrogen 1,2-shift from the C-17 position of *ent*-kaurenoic acid (156).⁶⁶⁾

17-Nor-16-azakauranes 190, 191, and 192 were found to inhibit gibberellin production of *Gibberella fujikuroi*.⁶⁷⁾ Isolation of a unique spirosecokaurane, shikodonin (193), and its structure determination were published.⁶⁸⁾

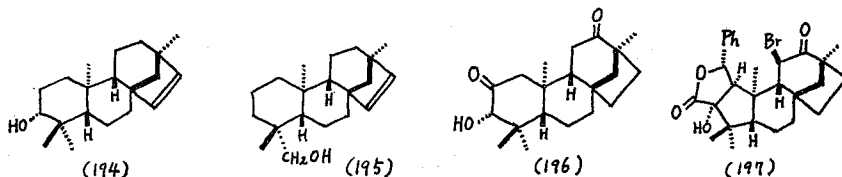


X. BEYERANE DERIVATIVES



(272)

ent-Beyer-15-en-3 β -ol (**194**), which was the first to be found from natural source, was isolated together with the known diterpenes, erythroxyol A (**195**) and *ent*-kaur-16-en-19-ol (**155**) from *Helichrysum dendroideum*.⁵⁴⁾ A mixture of the ketol **196** and benzaldehyde in aqueous ethanol on treatment with dil. NaOH in the presence of oxygen afforded a lactone, whose 11-bromo derivative was subjected to X-ray analysis to determine the structure as **197**.⁶⁹⁾



A total synthesis of 15-beyerene (**201**) *via* a sequence of reactions including a photochemical cycloaddition of vinyl acetate on the $\alpha\beta$ -unsaturated ketone **198** and a Wagner-Meerwein type rearrangement of the diols **199** and **200** as the key steps was achieved.⁷⁰⁾ The outline is shown in Chart 5.

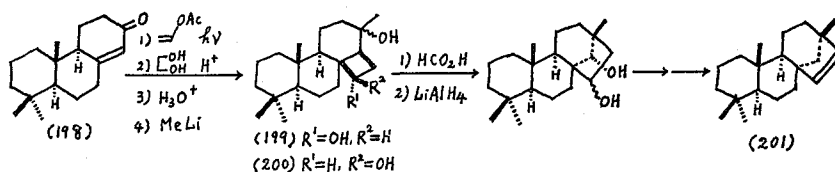
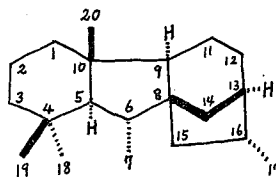


Chart 5

XI. GIBBERELLANE DERIVATIVES



Gibberellane

The photochemical reaction of 3-dehydrogibberellin A₁ (**202**) gave the $\Delta^{3,4}$ -unsaturated-3,4-seco-3-aldehyde **203** in good yield. This aldehyde **203** represented a suitable key compound for a recyclization reaction sequence to dihydro-gibberellin A₁ (**204**) and gibberellin C (**205**) as shown in Chart 6.⁷¹⁾

Photosensitive protection of carboxyl group as the *p*-methoxyphenacyl ester and the synthesis of three O-methyl derivatives (**206**–**208**) of gibberellin A₃ were published.⁷²⁾

Naphthoic acid derivatives **209** and **210** were converted into trichloroacetate and dichloroacetate derivatives and then to diazoketones, **211**–**214**. The acid-catalyzed cyclization of these substrates to the dienones, **215**–**218**, respectively, was studied. These dienones are suitable compounds for the synthesis of 13-hydroxygibberellins.⁷³⁾

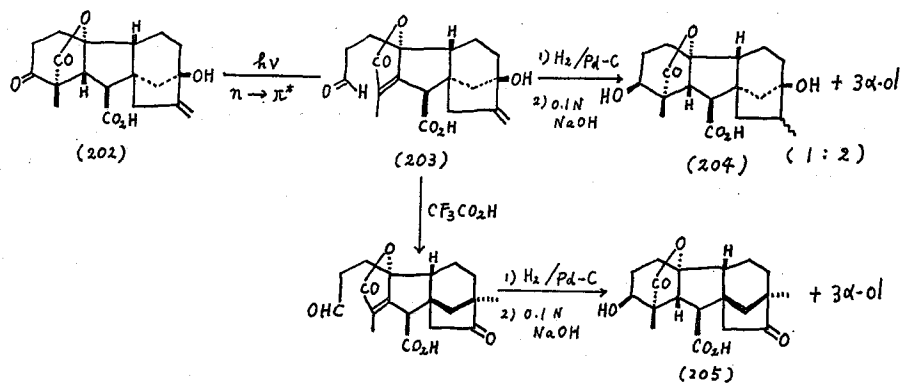
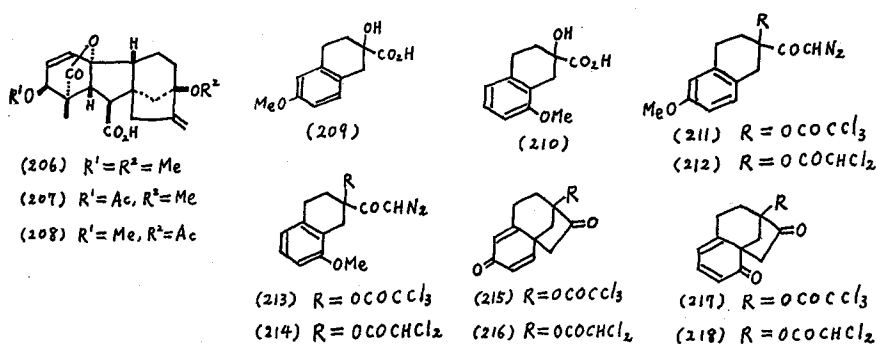


Chart 6



An approach to gibberellins utilizing the stereocontrolled bicycloannulation was published.⁷⁴⁾ The outline is shown in Chart 7.

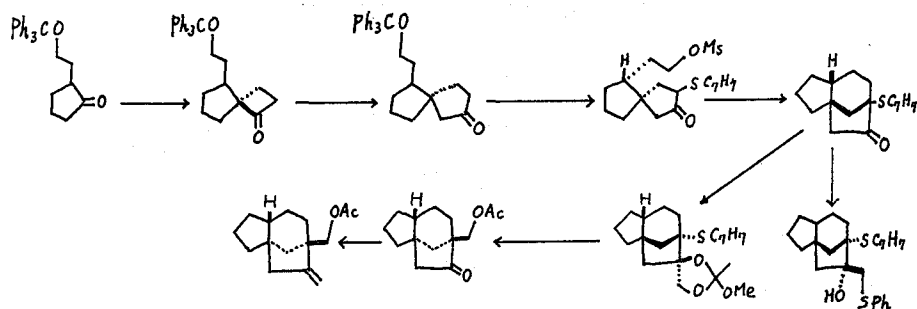


Chart 7

The C-20 carbon atom of the C₂₀ gibberellins was shown to be evolved as carbon dioxide during the biosynthesis of the C₁₉ gibberellins by *Gibberella fujikuroi*. It was

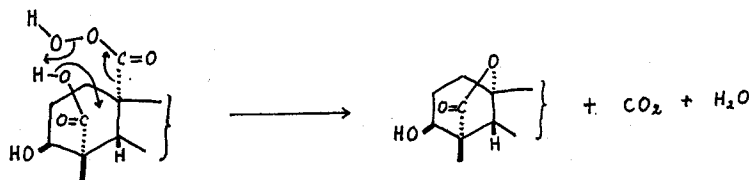
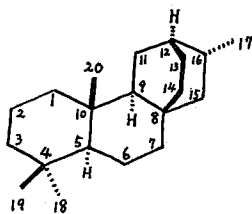


Chart 8

suggested that the decarboxylation might involve the decomposition of a C-20 peracid by either a radical or ionic mechanism (Chart 8).⁷⁵⁾

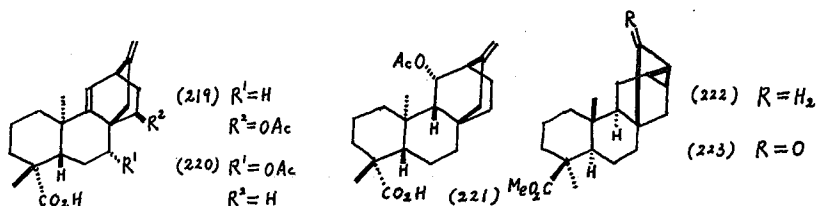
XII. ATISANE DERIVATIVES



Atisane

Three new atisane type diterpenoids, **219–221**, were isolated from *Garuleum sonchifolium*.⁷⁶⁾

The ¹³C NMR spectra of methyl trachylobanate (**222**) and ketone **223** were interpreted by comparing the ¹³C shielding trends with those of 12 model tricyclo-[3.2.1.0^{2,7}] octanes.⁷⁷⁾



As a rebuttal for non-equilibration of atisine epimers **224** and **226**, an alternative proposal involving rapid interconversion between two epimers *via* a zwitterion **225** was made.⁷⁸⁾ (See Chart 9.)

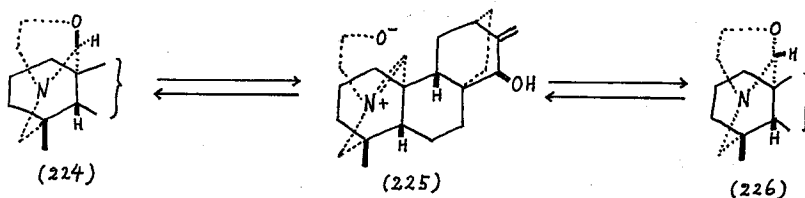
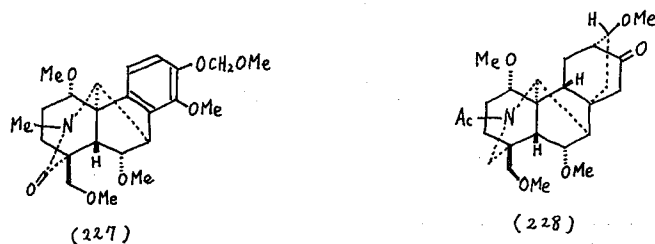
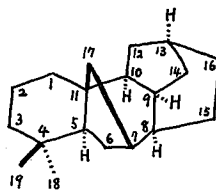


Chart 9

The key intermediate **228** for the total synthesis of 13-desoxydelphonine and chasmanine (**179**) was synthesized from **227**.⁷⁹⁾



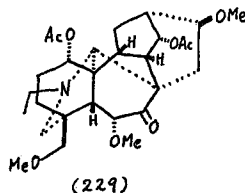
XIII. ACONANE DERIVATIVES



Aconane

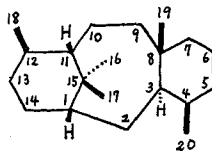
Some reactions of anhydrodiacetyldecosine(anhydrodiacetyl-lucaconine) (229) and its derivatives were described and the reaction products were shown.⁸⁰⁾

A model experiment on the construction of the C/D ring system of chasmanine (179) was published.⁶³⁾



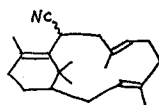
(229)

XIV. TAXANE DERIVATIVES



Taxane

A synthesis of a seco-taxane derivative 230 based on biogenetical consideration has been reported.⁸¹⁾

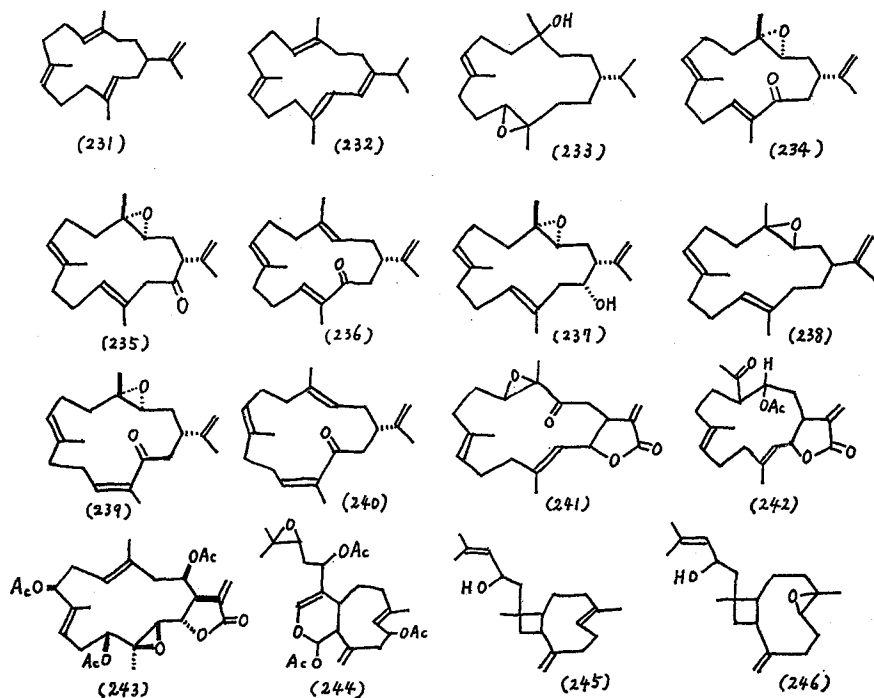


(230)

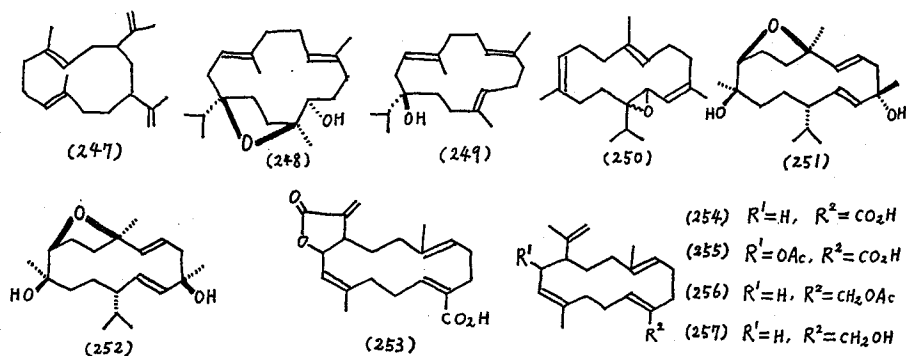
XV. THE OTHERS

A number of diterpenes have been isolated from marine sources, especially soft corals. Thus, two cembrene hydrocarbons, 231 and 232, from the *Nephthea* sp.,⁸²⁾ trocheliophorol (233) from *Sarcophyton trocheliophorum* and *S. decaryi*,⁸³⁾ compounds,

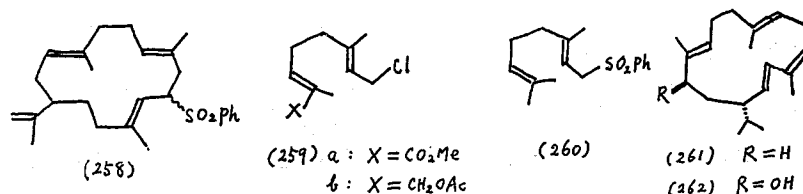
231 and 234–240, from an unidentified soft coral,⁸⁴⁾ compounds 241 and 242 from a soft coral of the genus *Lobophytum*,⁸⁵⁾ crassolide (243) from *L. crassum*,⁸⁶⁾ xeniculin (244), xeniaphyllenol (245), and xeniaphyllenol-oxide (246) from *Xenia macrospiculata*⁸⁷⁾ have been isolated.



The structure of an irregular twelve-membered-ring diterpene, cubitene (247), from a termite soldier *Cubitermes umbratus* was determined by an X-ray analysis.⁸⁸⁾ Incensol (248) and a new cembrenol 249 were isolated from the resin of *Boswellia carteri*.⁸⁹⁾ Serratol (250) was isolated from *B. serrata*.⁹⁰⁾ Two new diterpenoids were isolated from Greek *Nicotiana tabacum*. One of them was shown to be 251 by synthesis and X-ray analysis, while the other was tentatively assigned the structure 252 by spectroscopic means.⁹¹⁾ Anisomelolide (253), malabaric acid (254), 2-acetoxymalabaric acid (255), anisometyl acetate (256), and anisomelol (257) have been isolated from *Anisomeles malabarica*.⁹²⁾

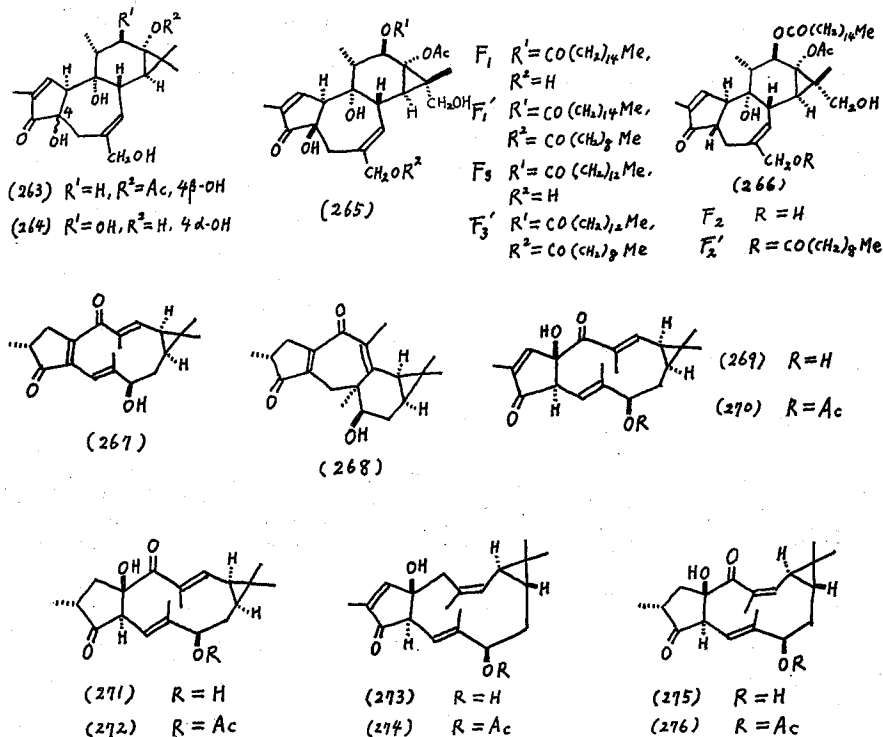


The cembrene derivative **258** has been prepared from the two geranyl units **259** and **260**.⁹³⁾ Regio- and stereoselective oxidation of compound **261** by selenium dioxide in acetic anhydride-acetic acid into **262** was reported.⁹⁴⁾



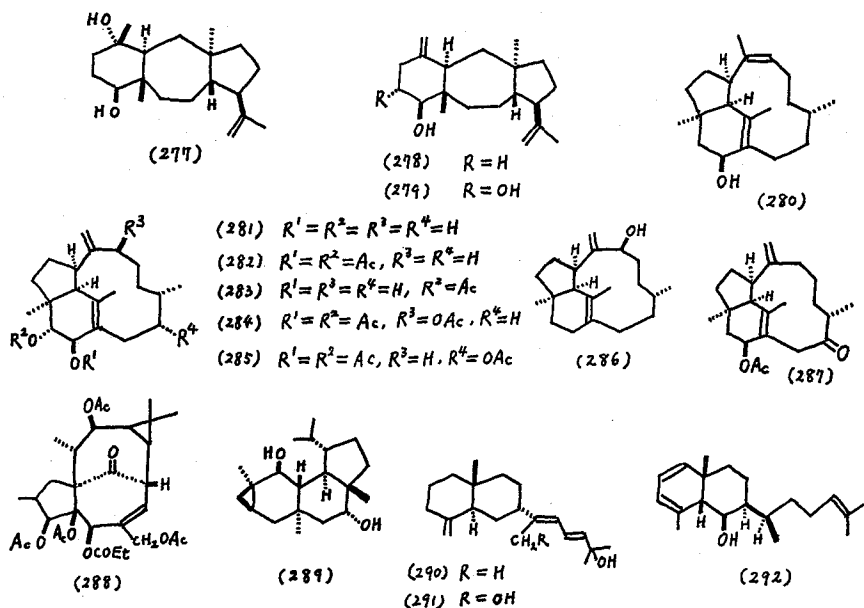
Carbon-13 nuclear magnetic resonance spectra of some fourteen-membered macrocyclic diterpenes were investigated in detail.⁹⁵⁾

The structure of prostratin (**263**) was investigated by overlapping Patterson peaks and direct methods on the X-ray analysis.⁹⁶⁾ Chemical ionization mass spectra of esters of **4a**-phorbol (**264**) were reported.⁹⁷⁾ From the roots of *Croton flavens*, three highly irritant and tumor promoting Croton factors F_1 – F_3 and the corresponding three cryptic Croton factors F_1' – F_3' were isolated and characterized as novel esters of 16-hydroxy- and 4-deoxy-16-hydroxyphorbol, respectively, as shown in **265** and **266**.⁹⁸⁾ Irradiation of bertyadionol (**267**) resulted in a single photoisomer **268**, while related compounds, diterpene B (**269**), its acetate **270**, diterpene D (**271**), and its acetate **272**, when photolyzed, underwent E→Z isomerization of the conjugated bond and epimerization about one center of the cyclopropyl moiety to give **273**, **274**, **275**, and **276**,



respectively.⁹⁹⁾ The structures **268** and **276** were further confirmed by X-ray crystallographic analysis.¹⁰⁰⁾

Three new diterpenes, **277–279**, were isolated from *Clavularia inflata*.¹⁰¹⁾ A new trinervitene, isotrinervi-2 β -ol (**280**), was isolated from the nasute termite *Trinervitermes gratus*.¹⁰²⁾ The frontal gland secretion of the soldiers of *Nasutitermes rippertii* was found to contain seven trinervitene derivatives **281–287**.¹⁰³⁾ A new diterpene **288** was isolated from *Euphorbia poissonii*.¹⁰⁴⁾ Structure of a novel carbon skeletal diterpene 2,9-dihydroxyverrucosane (**289**) was elucidated on the basis of chemical and spectral evidence.¹⁰⁵⁾ Two new diterpenes, **290** and **291**, were isolated from a soft coral, *Lobophytum hedleyi*.¹⁰⁶⁾ The related diterpenoid, dictyolene (**292**) and its C-11 epimer were totally synthesized from *m*-toluic acid.¹⁰⁷⁾



Base-induced rearrangement of sphaerococcenol A (**293**) gave rise to a compound whose structure was determined as **294** on the basis of chemical and spectroscopic evidence. A mechanism shown in Chart 10 has been proposed.¹⁰⁸⁾

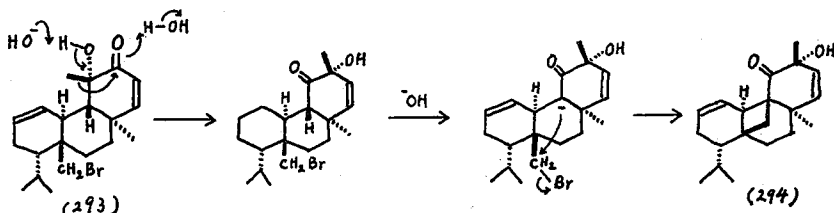
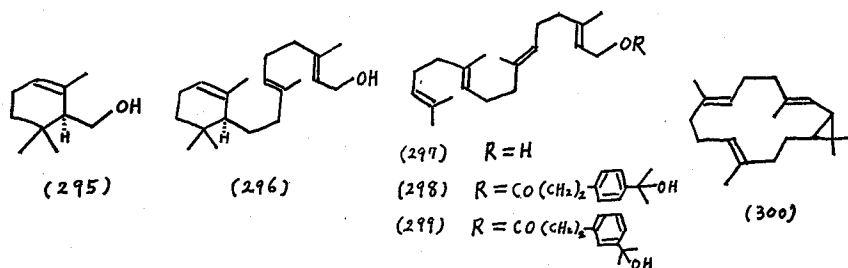


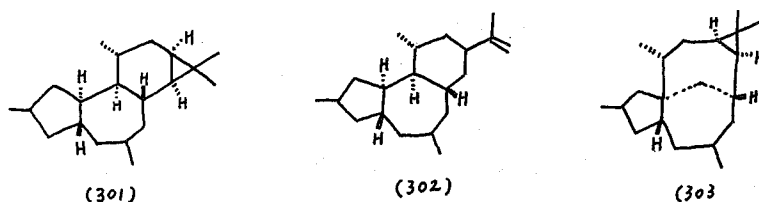
Chart 10

The synthesis of optically active natural caulerpol (**296**) from (S)-(-)- α -cyclogeraniol (**295**) has been reported.¹⁰⁹⁾



Template-directed epoxidation of flexible polyenes, specially all *trans*-farnesol and all *trans*-geranylgeraniol (297) was published. Thus, the results obtained from the epoxidation of 298 and 299 revealed some remarkable features of the conformational preferences of the molecules.¹¹⁰ In the studies on biosynthesis of the diterpene phytoalexin, casbene (300), casbene synthetase was partially purified and characterized.¹¹¹

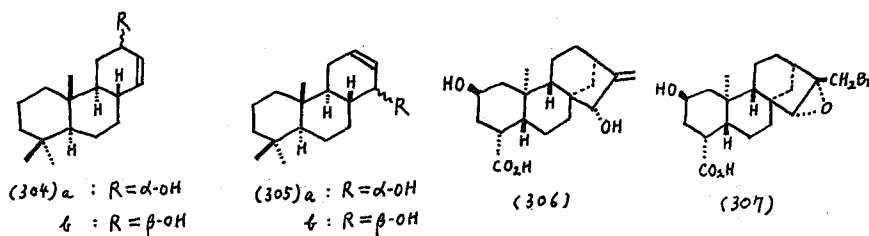
A review dealing with the chemistry, distribution, and biological activities of the "tiglane" (301), "daphnane" (302), and "ingenane" (303) diterpenes was published.¹¹²



A review with 47 references titled "Diterpenoids" has been published by Japanese authors.¹¹³ In a review article dealing with synthesis of insect pheromones, description on the synthesis of cembrene has appeared.¹¹⁴ Trinervitene derivatives along with clerodane derivatives were described in a review article on the chemical ecology.³⁷ A review on diterpene alkaloids has been published in Japanese.¹¹⁵ There is a paper titled "The alkaloids of *Delphinium biternatum*".¹¹⁶

ADDENDA

The mass spectra of the podocarpenols, 304 and 305, were investigated.¹¹⁷ Oxidation of atractyligenin methyl ester (306) with chromic acid gave selectively 15-oxo-derivative, whereas oxidizing the oxirane 307 with Jones reagent and treating the resulting 2-oxo-product with Zn dust and alkali gave the 2-oxo-derivative of 306.¹¹⁸



Two reports concerning the photosensitized oxidation of abietic acid were published.
119,120)

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